

## **Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)**

### **1 Introduction**

Energy dispersive x-ray fluorescence spectrometry (EDXRF) is a technique that can be used for the non-destructive elemental analysis of a wide variety of materials for elements ranging in atomic number from fluorine to uranium. Microspot x-ray fluorescence spectrometry (micro-XRF) is used for the analysis of samples that are too small for standard x-ray fluorescence analysis methods. Both EDXRF and micro-XRF can be used to characterize the major, minor, and trace elemental constituents present in solid and liquid samples.

### **2 Scope**

This document applies to personnel using the associated instrument(s)/equipment in the following disciplines/categories of testing: general physical and chemical analysis in support of metallurgy, anthropology or general chemistry examinations. This procedure serves as a general guideline for all FBI Laboratory procedures that involve the use of x-ray fluorescence spectrometry (XRF) analyses using energy dispersive detectors. (Wavelength dispersive detectors are not included in this standard operating procedure, SOP.)

Application of this SOP to forensic materials requires knowledge of general concepts of XRF analysis. Methods requiring analysis by XRF require operational proficiency of each instrument employed. This knowledge can be obtained from the references provided, training from manufacturers or principle operators within the unit, or schools covering theory or instrument operation.

General procedures for compositional analysis by EDXRF and micro-XRF are described below. Operational procedures for specific instruments are detailed in supplemental SOPs.

### **3 Principle**

XRF has its basis in quantum mechanics. An incident x-ray beam is used to eject core electrons from the atoms comprising the sample. Subsequent relaxation from the excited state results in emission of x-ray photons (x-rays), each with an energy that is characteristic of the element emitting it. Each photon striking the detector generates an electronic reaction that is converted to

a digital signal which is processed to determine the energy of the incident photon. Many such emission and collection events are measured during a single experiment. The spectral output is a histogram displaying the number of photons (or “intensity”) collected at each energy level over the time interval of the test. These relative intensities are the basis for determining the concentrations of each detected element in the sample.

Micro-XRF is a modification of standard EDXRF in which the x-ray beam is focused down to a small spot size. This can be accomplished using a beam collimator or a poly-capillary or mono-capillary x-ray lens. Such configurations permit elemental analysis of samples as small as the incident spot size.

#### **4 Specimens**

Virtually any liquid or solid sample can be analyzed by this method. Particles as small as 50  $\mu\text{m}$  in diameter can be examined using micro-XRF. Since the incident x-rays will interact with the sample surface, any surface coating or contamination will be measured during the procedure. Specimens may need to be cleaned or ground to measure underlying layers or base material.

For quantitative analysis, specimens must be prepared so that they have a flat, smooth surface and be sufficiently thick to accommodate the entire x-ray interaction volume.

In the case of liquid samples, a plastic cup can be used to contain the sample. Depending on the orientation of the x-ray tube and detector, either the flat surface of the liquid will provide the required analysis surface or the sample will be measured through a layer of polymer film.

#### **5 Equipment/Materials/Reagents**

- a. Energy dispersive x-ray fluorescence spectrometer, such as:
  - Thermo QUANT’X X-ray Fluorescence Spectrometer
  - Bruker M4 Tornado Micro X-ray Fluorescence Spectrometer
  - Olympus Delta Premium Handheld X-ray Fluorescence Spectrometer

The choice of instrument to use will depend on the desired measurement environment, the available amount and particle size of the sample, and the elements to be measured. Each EDXRF instrument has different capabilities to measure major and minor alloying elements and trace elements in different matrices. Refer to the individual instrument SOP for known limitations. Additional capabilities can be demonstrated on a case-by-case basis by appropriate validation.

- b. Calibration standard(s) appropriate for the specific instrument used.
- c. Mounting materials (optional, depending on sample) such as:
  - Graphite stubs
  - Durotak sample mounting adhesive
  - Plastic sample cups (liquid samples)
  - Chemplex X-Ray Mylar (2.5µm thick) or polypropylene film (6.3 µm thick) or similar
- d. Certified reference materials (CRMs), if an alloy class comparison, elemental quantitation, or the absence of a specific element is to be reported.

## 6 Standards and Controls

Each EDXRF instrument requires energy adjustment (sometimes referenced as “calibration” or “validation” by the instrument manufacturer) to coordinate the electronic signal from the detector with known emission energies from standard reference materials and to verify the energy resolution. The required performance check standard is listed in each instrument SOP.

CRMs are often used to demonstrate the discernment of major, minor, and trace elements in alloys similar to the sample under the same measurement conditions. For quantitative analysis, validation will be performed according to the *FBI Laboratory Operations Manual (LOM)* and *Chemistry Unit Quality Assurance and Operations Manual (CU QAM)* using appropriate CRMs.

XRF instruments are not calibrated by Chemistry Unit personnel. Adequate instrument performance is demonstrated prior to case work by performing a verification or energy adjustment routine. At a minimum, such a performance check is completed each day prior to the instrument being used for case work. In addition, energy adjustment should be performed when the spectrum peaks become shifted from their theoretical energy positions by more than 0.05 keV. A record of the performance check is retained near the instrument, in either electronic or paper form, to track historical performance.

## 7 Sampling

If large numbers of physically indistinguishable samples are received for compositional analysis, a sampling plan may be employed for testing. If the sampling plan will be used to make an inference about the population, then the plan will be based on a statistically valid approach. All of the samples may be tested at the examiner's discretion. For bulk samples, like soil or fines, the

material should be mixed until it appears visually homogeneous before performing sampling. Any sampling plan and corresponding procedure used will be recorded in case notes.

## 8 Procedure

### 8.1 Basic Operation

The basic operation of each individual instrument is detailed in the instrument SOP. The general steps for performing XRF analysis follow:

- a. Run the instrument performance check routine. File one copy with the instrument performance records.
- b. Prepare and insert the specimen(s).
- c. Apply the desired atmospheric environment: air, helium, or vacuum. Do not perform evacuation on unconstrained fine powders or on liquid samples. Fine powder can be protected from disseminating under vacuum if contained in a sample cup with a perforated film cover.
  - i. Where low atomic number (low Z) elements such as sodium and silicon are present, attenuation of the fluorescent x-rays produced will occur in air and dramatically increase the minimum detectable concentration of these elements. Typically, samples are analyzed under a vacuum of 1 torr or less (standard atmospheric pressure is 760 torr) to optimize the detection limits of low Z elements and to eliminate argon x-ray fluorescence which occurs as the x-rays pass through air.
  - ii. Helium is useful for measuring low Z elements in liquids because it is a poor x-ray absorber and does not contribute interfering signal.
  - iii. In samples where evacuation is not possible (e.g., fine powder or liquid), analysis will be conducted in air or helium atmosphere.
  - iv. For samples where low Z elements (F through Ca) are not present or relevant, analysis in air is acceptable.
- d. Adjust instrument conditions to best reveal the analytes (elements) of interest. This may be an iterative process. Selection of x-ray tube voltage and filtering is dependent upon the sample composition and the objective of the analysis. Choice of the optimal conditions for a given analysis requires experience and a basic knowledge of x-ray physics. Suitable tube current is dictated primarily by the need to have a sufficient count rate to collect a spectrum.

- i. If the compositions of two specimens are to be compared, analyze them both under the same instrumental conditions.
  - ii. If a specimen is to be compared to an alloy class or classes, analyze appropriate CRMs under the same instrumental conditions as the unknown specimen.
  - iii. If the absence of an analyte is under consideration, establish a limit of detection (LOD) for that analyte in a similar matrix under the same instrumental conditions.
  - iv. If quantitative compositions are to be reported, validate the analytes of interest in a similar matrix using CRMs according to the LOM and CU QAM.
- e. Acquisition duration will depend on the conditions chosen and the sample area exposed to the incident beam, but must be adequate to acquire sufficient counts for analysis. The acquisition time can be extended to optimize spectrum clarity or shortened to enhance collection efficiency based on the requirements of the case.
- f. Ensure the instrument identification and the operating parameters are recorded on the printed spectra or elsewhere in the case notes.

## 8.2 Spectral Analysis

Determination of the elements detected in a spectrum requires analysis of the peak shapes and energy positions, the relative heights of adjacent peaks, consideration of the effects of secondary and tertiary fluorescence and other x-ray/specimen interactions. System peaks, sum and escape peaks, Rayleigh and Compton scattering and diffraction may also contribute peaks to the spectrum and should be considered when interpreting spectra. Some XRF systems have software that can accurately identify the escape and sum peaks in a spectrum. The peak identification system resident in the instrument software can be augmented by analyzing CRMs of similar composition to the specimen of interest.

## 8.3 Quantitation of Data

In general, x-ray spectra are not used to generate quantitative data. However, the spectra acquired from a sample can be processed to yield weight concentrations of the elements detected. Different XRF instruments employ different software routines to quantitatively process spectral data. If numerical compositional data is to be reported, validation must be performed on the same instrument under the same operating conditions using CRMs with a matrix similar to that of the specimen of interest.

## **9 Instrumental Conditions**

Instrument conditions will vary depending on the instrument and application. See individual instrument SOPs and 8.1 Basic Operation.

## **10 Decision Criteria**

### **10.1 Instrument Performance**

Instrument performance is demonstrated during the instrument performance check. Energy adjustment of the instrument will be undertaken whenever the measured x-ray peak positions differ by more than 0.05 keV from their theoretical positions.

### **10.2 Qualitative Analysis**

Peak identification on XRF spectra requires a thorough understanding of x-ray physics, instrument performance and potential artifacts. Although instruments provide peak identification software, the analyst is required to interpret the validity of the suggestions produced by programs using libraries of x-ray energy lines. In addition:

- a. Comparisons between specimens must consider possible surface or embedded contamination, variations in surface topography between specimens and any variation in the as-manufactured homogeneity of pristine specimens.
- b. Comparison to an alloy class or classes must consider the factors above and the possibility of overlapping compositions among alloy classes. Although it may be possible to demonstrate that a specimen is of similar composition to a particular alloy class, it may be impossible for XRF to reveal whether a material was produced to a particular specification.
- c. If the absence of an analyte is under consideration, the validated LOD for that analyte in a similar matrix under the same instrumental conditions will determine the decision criteria.

### **10.3 Quantitative Analysis**

If quantitative compositions are to be reported, a CRM standard (selected by alloy) is used to check the accuracy of the quantitative analytical results (see 8.3 Quantitation of Data). If the measured concentrations of the major elements of interest deviate by more than 15% from the

certified values, the analysis should be rerun as systematic errors may be present. It is also noted that some element peaks may be overlapped by a major constituent rendering them indistinguishable. For example, the manganese peaks in stainless steel alloys are masked by those of chromium and iron. In such instances, any concentration results generated for the overlapped, minor constituent element should be regarded as no more than semi-quantitative in nature. If quantitative results are required, another method of analysis will be chosen.

## 11 Calculations

Calculations for establishing relative concentrations of elements in a measured sample are embedded in quantitation software routines of each XRF instrument. The internal routines are verified by CRMs as described above.

The expected position of escape and sum peaks on the energy axis can be calculated if they are not automatically generated by instrument software:

- a. For instruments using silicon-based detectors, an “escape peak” may appear at 1.740 keV less than the energy peaks of the major constituents.
- b. “Sum peaks” may appear at an energy equal to the sum of the peak energies of major constituents. For example, in a brass alloy with high zinc content, sum peaks can be seen at double the Cu K $\alpha$  energy, double the Zn K $\alpha$  energy and at the Cu K $\alpha$  + Zn K $\alpha$  energy.

## 12 Measurement Uncertainty

Typically, XRF is not used for quantitative analysis. Should quantitative reporting be required, the measurement uncertainty will be estimated in accordance with *Chemistry Unit Procedures for Estimating Measurement Uncertainty* in the CU QAM.

## 13 Limitations

The physical interactions of incident and emitted x-rays with the different components of an x-ray measurement system, including the measured sample, must be taken into account when analyzing XRF spectra:

- a. The detection limit of an element is dependent upon its atomic number, the matrix material, the analysis atmosphere, the presence of overlapping element energy peaks,

acquisition time, any filters used and other factors. Parts per million (ppm) level detection limits are readily obtained in some situations. More commonly, the practical detection limits in metal alloys range from ~0.01 - 0.1 weight percent depending on the matrix and the element being analyzed.

Where required, specific detection limits under a given set of analytical conditions can be estimated by analysis of compositionally similar CRMs containing known levels of the analyte of interest using identical instrumental conditions. The first eight elements of the periodic table (H, He, Li, Be, B, C, N, O) cannot be detected by XRF systems at any concentration.

- b. Unusually thin samples may result in skewing of the relative heights of the various energy peaks and thus cannot be reliably quantified. Similarly, a layered sample may produce a spectrum containing signal from the multiple layers.
- c. Peak identification in a spectrum can be complicated by the presence of diffraction peaks, scatter peaks associated with the x-ray tube target material, and other system peaks as discussed in 8.2 Spectral Analysis. For example, using Mylar film to support a specimen may contribute a Ca peak to the spectrum. Organic matrices also generate high background scatter. Analyzing a known material with a matrix similar to the specimen can often help identify these artifact features in a spectrum.
- d. On-board peak identification routines compare measured energy intensities with the known characteristic energies emitted by elements. The analyst must take into account the likelihood of the presence of any particular element. For example, in a manganese standard, an automated peak identification routine may indicate that an energy peak at 6.49keV could be a Dy  $L\alpha$  line or a Mn  $K\beta$  line. The analyst should recognize that dysprosium is not likely to be present based on its rarity in the earth and upon the absence of additional Dy spectral emissions.
- e. Different types of x-ray detectors have different limitations of performance. Solid state detectors using lithium-drifted silicon crystals (SiLi) require sufficient cooling to retain chip integrity and provide adequate energy resolution (e.g., Peltier cooling). Silicon drift detectors (SDD) do not need to be cooled as severely to achieve adequate resolution, but they provide relatively poor sensitivity for high energy x-rays. This effect can be mitigated somewhat by choosing optimum tube excitation and filtering conditions during measurement.
- f. X-ray fluorescence energy spectra are subject to numerous, but well documented, interferences from other element characteristic energies. The following common



interferences are known for spectra collected using SiLi or SDD energy dispersive detectors. The presence of these interfering species can usually be determined from examination of the affected peak series, the peak height ratios and the presence of higher energy peaks that will normally accompany the interfering species.

Element	Interferences
F (K lines)	Fe (L lines)
Na (K lines)	Cu (L lines)
Mg (K lines)	As (L lines); Tb (M lines)
Al (K lines)	Br (L lines); Tm, Yb (M lines)
Si (K lines)	Rb (L lines); Sr, W (M lines)
P (K lines)	Zr (L lines); Ir (M lines)
S (K lines)	Mo (L lines); Pb (M lines)
Cl (K lines)	Rh (L lines); Ru (L lines)
K (K lines)	In (L lines)
Ca (K lines)	Te (L lines); Sb (L lines)
Ti (K lines)	V-K $\alpha$ ; Ba (L lines); La (L lines)
V-K $\beta$ line	Cr-K $\alpha$ line
Cr-K $\beta$ line	Mn-K $\alpha$ line
Mn-K $\beta$ line	Fe-K $\alpha$ line
Fe-K $\beta$ line	Co-K $\alpha$ line
Co-K $\beta$ line	Ni-K $\alpha$ line
Ni-K $\beta$ line	Cu-K $\alpha$ line
Cu-K $\beta$ line	Zn-K $\alpha$ line
As (K lines)	Pb (L lines)

## 14 Safety

- Wear an x-ray film badge or dosimeter when operating instruments that generate x-rays. The instruments have protective enclosures and internal safety interlocks to prevent inadvertent x-ray radiation exposure. Never bypass or disable safety interlocks on instruments.
- XRF detector windows are comprised of beryllium and are extremely delicate. In the event of damage to the window, the beryllium dust created could pose an acute health

hazard. If this occurs, seal the chamber and seek assistance from the Laboratory Health and Safety Group.

## 15 References

Jenkins, R., *X-ray Fluorescence Spectroscopy*, Wiley Interscience, New York 1988

Jenkins, R., Gould, R.W. and Gedcke, D., *Quantitative X-ray Spectrometry*, 2<sup>nd</sup> ed., Marcek Dekker, Inc., New York 1995

Buhrke, V.E., Jenkins, R., Smith, D.K., *Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis*, Wiley-VCH, New York 1998

Margui, E. and Van Grieken, R., *X-Ray Fluorescence Spectrometry and Related Techniques*, Momentum Press LLC, New York 2013

*Chemistry Unit Quality Assurance and Operations Manual*, Federal Bureau of Investigation, Laboratory Division, latest revision

*FBI Laboratory Operations Manual*, Federal Bureau of Investigation, Laboratory Division, latest revision

*FBI Laboratory Quality Assurance Manual*, Federal Bureau of Investigation, Laboratory Division, latest revision

Rev. #	Issue Date	History
0	08/18/2014	Original issue. Relevant general information was taken from 18-1 Operation of the EDAX Eagle III XXL Micro X-Ray Fluorescence Spectrometer and 20-1 Operation of the Thermo QUANT'X X-Ray Fluorescence Spectrometer for specific EDXRF instruments.
1	03/02/2018	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 25 and is now designated Metal 500. Included referenced acronym in title. Added personnel to section 2. Made minor editorial corrections and terminology changes throughout document. Deleted obsolete equipment in section 5. Incorporated section 7 into section 6 and renumbered subsequent sections. Added requirement for sampling plan retention in section 7. Added section 8.1.e to clarify operation. Revised description of instrument performance check in section 10.1. Updated section 13 to clarify instrument limitations. Deleted obsolete section 14.c. Added additional references to section 15.

**Approval**

Redacted - Signatures on File

Metallurgy  
Technical Leader

Date: 02/28/2018

General Chemistry  
Technical Leader

Date: 02/28/2018

Anthropology  
Technical Leader

Date: 02/28/2018

Chemistry  
Unit Chief

Date: 02/28/2018

Trace Evidence  
Unit Chief

Date: 02/28/2018

**QA Approval**

Quality Manager

Date: 02/28/2018